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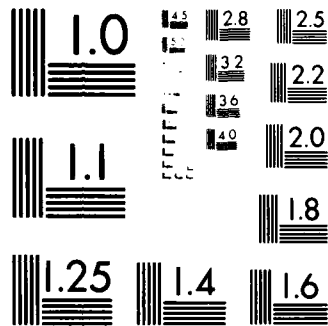
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TECHNICAL REPORT NO. 09

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THIN FILMS: OPPORTUNITIES FOR LANGMUIR-BLODGETT
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M. B. Biddle and S. E. Rickert

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Abstract

Oriented films possessing dipole moments have seen increasing use of their piezoelectric and pyroelectric properties in pressure, acoustic, thermal, and optical devices. The performance of these devices in many applications is enhanced by thin film technology. The current thin film technology and possible opportunities for the developing Langmuir-Blodgett thin film deposition technique is reviewed with an emphasis on applications.

Introduction

Piezo- and pyroelectrics were first utilized in simple pressure and thermal detectors. These materials were typically in "bulk" form, perhaps cut from single crystals, ceramics or even plastics. The success of these devices prompted the desire to extend their use to more demanding applications requiring higher sensitivity, higher frequency operation and

smaller physical size. Thin film technology for piezo- and pyroelectrics was conceived to satisfy these desires for improved performance.

The operating frequency of piezoelectrics is determined by the transducer thickness. Therefore, the thinner the transducer, the higher the optimum operating frequency. In pyroelectrics, the noise equivalent power decreases and the responsivity increases as the film thickness is reduced. The incentive for obtaining thin films is evident from these two factors alone.

Materials engineers have developed vapor deposition and sputtering techniques to apply ceramic thin films to substrates. Polymer films, primarily polyvinylidene fluoride, have also been investigated and developed. However, these materials and techniques are not without their drawbacks and problems. Langmuir-Blodgett film deposition is an old technology which has recently experienced a renaissance of interest. This technology may provide significant improvements in many applications requiring finely-controlled, oriented, ultra-thin films.

This article examines the piezo- and pyroelectric phenomena and applications thereof. In particular, the importance of piezo- and pyroelectric thin films is discussed. Current thin film materials and processing technologies are surveyed with the intent of identifying areas where Langmuir-Blodgett films may be applicable.

Background

The Curie brothers, Pierre and Jacques, are credited with first discovering the piezo- and pyroelectric effect in the 1880's. In 1894, Woldemar Voigt established the relationships between piezoelectricity and crystal structure [1]. The essential requirement is the possession of a non-centrosymmetric structure exhibiting polarity. Of the 32 crystal classes, only 20 fit this requirement, as shown schematically in Figure 1. The model in Figure 2 illustrates the importance of the non-centrosymmetric structure [2-4]. In the centrosymmetric structure any inherent dipole moments cancel. Only a non-centrosymmetric will possess a net dipole moment.

The piezo- or pyroelectric effect originates simply from a change in the internal dipole moment of the material upon a pressure or temperature change. It is manifested as the creation of a detectable external electric field. In an insulator this electric field causes a surface charge compensation [5].

The simple bulk pyroelectric sensor depicted in Figure 3 will be useful in the development of the basic principles of piezo- and pyroelectricity. If the sandwiched material has polarization perpendicular to the electrodes, a bound surface charge of q will be developed:

$$q = A * P$$

where: A = surface area
P = total polarization

The total polarization can be written as:

$$P_s = E_b + P_S$$

where: = electric susceptibility
 E_b = any biasing field
 P_s = spontaneous polarization of the material

The current flow, I, is defined as:

$$I = dq/dt = A * dP/dt = A * d/dt (E_b + P_s)$$

where: t = time

Maintaining E_b , and P_s constant with respect to time:

$$I = A (E_b + P_s) dT/dt$$

where T = temperature

Without induced effects, the true pyroelectric current can be written as:

$$I = p * A * dT/dt$$

where p = p, the pyroelectric coefficient,
a material property

Now:

$$I = p * A * dT/dt$$

The resultant current is a function of the pyroelectric coefficient, the electrode area and the rate of temperature change [6]. Thus a signal must be

modulated or chopped in order for a piezo- or pyroelectric device to develop a current flow.

It is obvious that materials possessing piezo- and pyroelectric behavior can be readily used as sensors to detect changes in strain or temperature. Applications utilizing these effects in "bulk" specimens are varied and many. Piezoelectric transducers are used in phonograph cartridges, contactless switches, keyboards, microphones, speakers, sonar, mechano-electrical energy conversion, and electronics filters, just to name a few common examples [1,7-11]. Pyroelectric devices find use in such applications as intruder/burglar alarms, pollution monitoring, radiometers, pyrometers, vidicons, etc. [6,12]. Single crystals, ceramics and plastics have all found their way into these and other applications.

The use of thin films of these materials can result in improved performance in most of the above devices as well as extending their applicability to many more demanding areas. The optimum operating frequency of piezoelectric transducers is controlled by the transducer thickness. To minimize losses and obtain the widest fractional bandwidths, the thickness should be about one-half of the wavelength of the mechanical wave traveling in the transducer. Thus, as the desired operating frequency is raised, the transducer should be thinned. As a benchmark, at 100 MHz, the thickness should be in the 20 micron range [13-15]. High frequency applications will be discussed later.

The performance of the pyroelectric detectors already mentioned could be improved by the use of thin films solely due to the increase in

responsiveness of the devices [16-18]. However, thin films also reduce the noise equivalent power (NEP) of pyroelectric devices. This is the signal that must be generated in the device in order to overcome the noise generated at a given frequency (it is therefore simply equal to the noise present at a given frequency) [19-22]. These two improvements enable their use in more demanding applications as will be seen.

Besides the dimensional (thickness) requirements, most applications require high quality films of known and consistent orientation [13,14,39]. Unfortunately, as the thickness is reduced, the methods used to obtain these films increase in difficulty. The problem of substrate adherence becomes critical. The interface region and substrate effects become more important. In addition, impurities and defects have a more profound effect on the device performance. These considerations will be addressed with respect to materials in the next section.

Materials

Ceramics and single crystals

Probably the most noted single crystals are quartz and TGS (triglycine sulphate, $(\text{NH}_2\text{CH}_2\text{COOH})_3 \text{H}_2\text{SO}_4$). Quartz is primarily found in oscillator frequency controllers and wave filters due to its great stability and low dissipation [1]. However, cutting a single crystal into a thin film and

bonding to a substrate can prove rather difficult. TGS is most known for its use in infrared detectors where it is typically used in the form of a 10-30 micron thick disc cut from a single crystal which was grown from an aqueous solution. The cleaved disc must be ground and polished prior to use [19,23]. Its biggest drawbacks are its hygroscopic nature and its tendency toward spontaneous depolarization [6].

Ceramics came into use in the late 1940's with the discovery of barium titanate (BaTiO_3) [1]. This material was soon replaced in many applications by lead titanate zirconate (PZT) compositions possessing stronger piezoelectric effects and higher operating temperatures [9]. Of the numerous available ceramics, the nonferroelectric seem to get the most attention for thin film piezo- and pyroelectric applications. Among these are cadmium sulfide (CdS), zinc sulfide (ZnS), aluminum nitride (AlN), gallium nitride (GaN), and zinc oxide (ZnO). [24-29] Ferroelectric (and thus also piezoelectric) lithium niobate (LiNbO_3), lead titanate (PbTiO_3), BaTiO_3 , PZT, PLZT (PZT with lanthanum) and others have been successfully deposited and used in thin films as well [30-33].

Grinding and polishing thin plates cut from bulk specimens and subsequent attachment to a substrate has been replaced (in most cases) by more direct deposition procedures. Typical thin film deposition techniques include thermal evaporation, chemical vapor deposition (CVD) and several sputtering methods (e.g., dc diode, rf, triode and magnetron) [13,14,26,34]. The major requirement of any deposition procedure is that it provide a high resistance film of known and controlled crystallographic orientation. The

orientation achieved during the growth of the films controls the mode of the device response. For example, an ultrasonic transducer will generate longitudinal waves if the film has its c-axis (let us assume a hexagonal material) normal to the substrate and/or electrodes when a field is applied. A shear wave propagates if the c-axis is in the film plane. Figure 4 graphically depicts the theoretical responses of ZnS and ZnO for various angles [14,26]. Mixtures of waves can actually be produced. The importance of controlled orientation is evident. There are numerous parameters necessary to characterize a deposition that could possibly influence orientations [35]. Deposition temperature, deposition rate and substrate microstructure are among the key factors to be controlled.

Besides orientation concerns, the deposition process must be considerate of substrate effects [20,21,105], non-stoichiometric deposition, high temperature degradation of the assembly, intrinsic stresses [24,36,125], surface roughness and thickness uniformity. Non-stoichiometric depositions can result due to the fact that the temperature required for vaporizing these materials is greater than their decomposition temperature. The vapor phase is therefore composed of the elemental species, which have different vapor pressures. For instance, in CdS depositions, the sulfur has a higher tendency to reevaporate from the substrate and will be deficient in conditions using CdS as the only source. Adding an extra sulfur source and/or using the hot wall technique [27] are two methods employed to ease this problem.

High temperature deposition can damage the substrate and create significant stresses in the film leading to spurious and irreproducible

responses. The concern for stress accumulation and ultimate cracking of the film is greatest for films with substantially different thermal expansion coefficients from the substrate. These concerns have been addressed with investigations using laser annealing [32]. It is also claimed that, in general, acceptable depositions can be achieved at lower temperatures with sputtering versus CVD methods [37]. Surface roughness, as well, is more pronounced in CVD films and polishing is generally required. Smooth films are reported for sputtered films [29,37-39,105]. The preceeding brief discussion perhaps explains the current interest in sputtering of ceramic thin films.

Polymers

With the discovery of the piezoelectric effect in polyvinylidene fluoride (PVDF) [40], interest in the field of piezo- and pyroelectric polymers was greatly stimulated. Many workers have investigated these effects in other polymers with a lesser degree of success as is illustrated by Figure 5 [7,41-44]. The piezoelectricity (represented by the strain or d constant) is shown to be related to the dielectric constant. The planar zig-zag conformation of phase I PVDF belongs to the non-centrosymmetric polar group $mm2$, which possesses a strong dipole moment [45,46]. It has the greatest polymer response measured to date. For this reason there is a high concentration of effort into understanding the phenomena in PVDF [7,41,47-51,116,117,119,123,124].

The lure of polymers lies in their flexibility, ease of formation into thin films, low mass, and potentially low cost. The disadvantages include lower coupling factors, a lower temperature range, frequency dependences, and the requirement of relatively high poling fields. Despite limitations, there exist numerous applications exploiting their advantages [7,8,43,47,49,52-54].

Some typical thin polymer film fabrication methods are solvent casting, hot-pressing, machining, laser-evaporation, and stretching of blown or extruded films. The last method is probably the most widely used for PVDF as the stretching results in molecular orientation. The films are then heated under a constant d.c. field to increase the dipole orientation. The film fabrication method essentially mandates the subsequent adherence to a substrate. This by-passes many of the deposition concerns mentioned for ceramics, but adds new ones such as adhesive effects.

For completeness, the work in plastic/ceramic composites should be noted. Researchers, particularly at the Pennsylvania State University and the Naval Research Laboratory, have investigated these composites to take advantage of the high piezo- and pyroelectric properties of the ceramics, the low acoustic impedance of the plastics and thus the overall material design flexibility inherent in composites [55-59]. The samples are cut and ground as is usually done from bulk specimens. Thin film tapes of 0.1-0.2 mm have been developed, but this is magnitudes thicker than what is applicable to the devices presently discussed.

Langmuir-Blodgett films

In the 1930's Irving Langmuir and Katherine Blodgett collaborated to develop a method to deposit monomolecular layers onto solid substrates [60,61]. Briefly, an appropriate amphiphilic molecule (one possessing a hydrophobic tail and a hydrophilic head) is deposited onto a water surface, usually dropwise, via a volatile carrier solvent. It may spread to form a monomolecular layer. The layer is compressed to a quasi-solid, one molecule thick. If a suitable substrate is passed through the water surface while the surface pressure is maintained, a monolayer can be deposited with each vertical dip. The method is demonstrated in Figure 6. Conditions such as type of molecule, temperature, aqueous phase acidity, and dipping speed are very important parameters. These parameters are discussed in numerous references (for example, see references 61-65, 136 and 137).

As evident from the above and many other sources, the Langmuir-Blodgett (LB) film deposition technique is experiencing a significant resurgence of interest. The LB technique offers a means to deposit a highly oriented film of very controlled thickness. The "thinness" can obviously range from the molecular length on up, depending merely on the number of layers and the length(s) of compounds to be deposited. The nature of the film can be altered very easily (within limits) by simply altering the molecule to be deposited. This type of "molecular engineering" is very attractive to many technological and research areas, including electronics.

Films can be deposited in several modes, depending on the substrate surface treatment and dipping methodology as shown in Figure 7. This is a very important point for the devices in question. As is evident from the figure, a spontaneous polarization should exist in films of polar molecules deposited in the X or Z mode. With the Y mode no polarization will exist due to cancelation of the dipole moments by alternating layers. Fortunately, it has been shown the the molecular orientation can be controlled to give head-tail (X type) or head-head-tail-tail (Y type) structures [66]. A number of researchers have investigated the dipole effect in LB films already, with several mentioning piezo- and pyroelectric possibilities [63,67-71,122,128]. A Russian group has demonstrated piezo- and pyroelectric properties in multilayers of several types of molecules [72].

The typical materials of interest in this application of LB films would be fatty acids with at least one unsaturated site in their backbone available for polymerization. Much work has been done on non-polymerizable materials which suffer from poor mechanical properties and stability. Polymerization would not only increase the mechanical integrity of the final product but is probably a necessary step between layer depositions to keep the molecules oriented properly since hydrophobic tails do not necessarily like to attach to hydrophilic heads and visa-versa. Polymerizing each monolayer ties the molecules together and reduces or eliminates the possibility of the molecules turning around after deposition [66].

The need to obtain high quality thin films for electronics applications in general and for piezo- and pyroelectric devices in particular is an established fact. Methods and materials available for obtaining thin films

have been reviewed. Each technology has its advantages and limitations. The advancing LB technology possibly offers several advantages not currently available in the current arena. These stem from the ability to molecularly engineer films to a very precise chemical, morphological and physical degree.

The quality of a thin insulating film is evidenced by dielectric measurements, which should theoretically be thickness independent. Figure 8 shows the variation of the dielectric constant with thickness of ZnS films. The drop in dielectric constant as the film thickness decreases is attributed to structural porosity. The thickness at which the drop occurs depends on the deposition technique and conditions. Structurally perfect films of cadmium stearate have shown an unfailing dielectric constant down to one monolayer thickness (2.46 nm) [26,133]. Capacitors made with LB films of stearic acid have shown greater stability and reproducibility than those with native oxide layers [73].

Applications

Some of the device applications for piezo- and pyroelectric thin films will be discussed. Emphasis will be placed on the properties required of the thin films for optimum performance of the devices. Current materials will be presented and opportunities for technological impact from LB films will be explored.

Electromechanical and audio frequency transducers

Electromechanical applications include contactless switches, keyboards, coin sensors, strain transducers and any type of pressure sensors [1,7,8,74]. Film thickness is not very critical here. PVDF has been exploited in many of these devices due to its flexibility. Audio frequency transducers are used in microphones, speakers, electronics filters, hydrophones (sonar), and medical sensors as a few examples [7,75]. Again, PVDF is popular due to its flexibility and formability. For hydrophones and medical sensors it is particularly attractive due to its close impedance match to water. Ceramic plates require acoustic backing materials to compensate for their relatively high impedance. Film thickness and material properties are more critical here than with the electromechanical applications. LB films could offer impedance tailoring and fine control of response characteristics for applications such as filters, but in general this field is fairly well satisfied by traditional ceramic and plastic films.

Ultrasonic transducers

As the frequency increases, so does the necessity for thinner and higher quality films. A schematic of a simple bulk wave ultrasonic transducer assembly is presented in Figure 9. These devices were limited by the

abilities to make and bond films below 10-20 microns. As mentioned previously, this limited the frequency to the 100 MHz range for efficient transduction. Vacuum evaporated films of CdS were first used to push the useful frequencies higher. Later came sputtering techniques and ZnO with its higher coupling. Films of ZnS, AlN, and the niobates (such as lithium) have also been used but not as successfully due to their lower coupling efficiencies. Films of 1 micron thickness and frequencies of 1 GHz are now possible with ceramics [13].

PVDF has been touted for ultrasonic applications due to its flexibility, formability, low cost, and particularly its low acoustic impedance. As already mentioned it is a close match with water and does not require all the acoustic backing typical for ceramics to match their high impedance to that of water. These applications would be in the medical imaging and non-destructive evaluation areas [52,53,75-77].

Interest in surface acoustic wave (SAW) devices has increased in recent years for applications such as signal processing [13,24,78], highly sensitive pressure sensors [25], radar [1], and electronics filters [33,79-81]. A SAW device is depicted schematically in Figure 10. The surface wave generated by the interdigital transducer (IDT) can be altered by interaction with the piezoelectric. The need for uniform thin films is even greater for SAW devices than for bulk wave devices. Since this is an area containing many specific applications of interest, a sampling will be presented.

Das and Schumer demonstrated the signal processing functions of convolution and Fourier transformation using the diffraction of a HeNe laser

from SAWs propagating on LiNbO_3 . Their experiments were performed at 45 and 100 MHz. A schematic of their optical processor is reproduced in Figure 11 [78].

Kanda and Gross developed a high frequency response pressure transducer utilizing a SAW device. Their experiments were performed at a nominal frequency of 103 MHz. A schematic diagram of the test apparatus and a graph of the results is given in Figure 12. The authors reported high frequency response and high reproducibility using LiNbO_3 [25].

The deflection and modulation of optical guided waves has been demonstrated by several researchers. The lay-out of a deflection experiment performed by Kuhn and others at IBM is shown in Figure 13 [82]. The materials utilized by various researchers include quartz, LiNbO_3 , and PVDF [76,82-85].

Gaalema and others at Purdue modified a charge coupled device (CCD) by replacing the gate structure with a piezoelectric thin film of LiNbO_3 containing IDTs for use as a SAW. The structure, given the acronym SWICC for surface wave interaction charge coupling, is depicted in Figure 14. The authors claim higher resolution, larger information density, and higher frequency operation thanks to the SAW interaction [86].

The critical factors for these acoustic wave films are high resistivity, uniform controlled crystallographic orientation, uniform thickness, and controlled stoichiometry. The performance of these types of devices should be enhanced by the LB film deposition technology. Specifically, thinner

films of higher order, uniformity, and orientation should permit higher frequency operation. This would extend applications and improve resolutions in such area as acoustic imaging. An ultrasonic transducer using LB films has already been demonstrated with as few as 5 molecular layers [118]. The frequency limitations of current technologies is a noted problem [33,59,80].

The ultimate in high frequency demands on piezoelectric transducers may be photoacoustic microscopy which requires operating frequencies in the GHz region for adequate resolution of surface and sub-surface details. The gas-microphone method has been used but its resolution is limited by the frequency response of the microphone to less than 20 KHz. Sample size and shape is limited with this method as well. Piezoelectric detection offers much higher frequency operation and much less sample limitation. Thin films of ZnO, LiNbO₃ and PZT have been used in acoustic microscope components such as SAW devices or even directly bonded to the specimen [87-90]. The pyroelectric effect has been used for thermal-wave photoacoustic microscopy [91,92]. The oriented ultra-thin LB films are attractive here due to the very high frequency possibilities and the typically low acoustic impedance of LB materials.

Integrated piezoelectric silicon FET

Piezoelectric thin films have been combined with field effect transistors (FETs) to create hybrid structures by a number of research groups. Acronyms such as PI-FET and POSFET, for piezoelectric FET and

piezoelectric oxide semiconductor FET, have been affectionately assigned these composite structures as is the tradition in the electronics industry. The film can function in the semiconductor, substrate or insulator positions. A typical configuration is shown in Figure 15 [93]. Advantages claimed for ZnO films are compatibility with planar Si processing, separate optimization of the free-carrier transport and piezoelectric properties, and localization of strain sensitivity to a very small area. Applications for these type of devices include sensitive high frequency strain transducers [93], integrated silicon accelerometers [94] and transducer arrays for acoustic imaging [53].

The use of thin oxide and spin-coated polymer films as insulating layers in electronic devices such as FETs is well known. This is also an area where LB films have already been successfully incorporated as extremely thin high quality films. Some of the devices that have been demonstrated using LB films are MIM structures, MIS structures, diodes, and FETs [63-71,95-98]. This is thus an area where piezoelectric LB films may make a significant impact relatively easy.

Pyroelectrics

Pyroelectric sensors react to changes in detectable radiation. They have therefore found use in areas such as radiometry, pyrometry, thermometry, solar energy conversion, intruder/burglar alarms, pollution monitoring, and enthalpimetric sensors [6,12,17,126]. These detectors, sensors, and alarms

require fast response, short dead (saturation) times, and high sensitivity. All of these requirements point to thin films. A particularly fast response is required of IR detectors that are used in the detection of subnanosecond pulsed CO_2 lasers [16,22,99,121]. The solar energy converter is an example of an application utilizing non-linear effects to enhance efficiency. Each specific material would have a specific optimum thickness in this type of device.

These pyroelectric applications are fairly well serviced by the current materials such as BaTiO_3 , LiNbO_3 , LiTaO_3 , and TGS. However, as noted earlier, LB films could improve the response time, sensitivity, and NEP of these devices due to a lower thermal capacity of the thinner films. These benefits could be realized to an even greater extent in thermal imaging, which is a more demanding pyroelectric application.

There are two basic types of thermal imaging devices, the vidicon tube and the detector array. The pyroelectric vidicon operates similarly to the television vidicon except the photoconductive target is replaced by a pyroelectric target. An electron beam "reads" and neutralizes a target area which is then renewed by the modulated or chopped incoming radiation. Figure 16 presents the general concept of a vidicon. The most common pyroelectric target is TGS, typically a disc from a single crystal cut and polished to a thickness of 10-50 microns. Other materials that have been used to a lesser degree are TGFB, LiTaO_3 , PBZT, and PVDF [6,23,120].

One of the methods currently employed to improve resolution and contrast in pyroelectric vidicons is known as target reticulation. The idea is to

isolate domains of the target in order to lessen lateral thermal diffusion. Channels are cut in a grid pattern to effect the isolation. The channels must penetrate to the supporting substrate, which must be thin in order to avoid thermally loading the target. Also the channels must not be so wide as to significantly reduce the target area, otherwise they would offset the advantages. Ion milling has been used for TGS with reported success, as long as the material survives the process [23,100].

The other type of thermal imaging utilizes pyroelectric detector arrays. Hand-held imagers have been on the market for many years. A typical unit manufactured by Plessey Ltd., in Great Britain, uses an array consisting of 32 TGS detectors [6,23]. Honeywell Inc. has developed what they describe as "the nation's first experimental pyroelectric imager in a 10x32 element mosaic". They used a lithium tantalate pyroelectric sensor array combined with a CCD (similar to the work by the group from Purdue mentioned earlier). The complete solid state device forms a rugged package slightly over one inch long in its largest dimension [101].

The pyroelectric vidicons and the detector arrays compete with the delicate high-performance mercury cadmium telluride detectors that the military typically uses for its infrared imaging needs. The performance of the pyroelectric devices is somewhat inferior to the cryogenically cooled units, but their ambient operation offers significant advantages such as smaller size, greater dependability, and lower cost. Pyroelectric vidicons are now capable of thermal imaging pictures comparable in quality to visible television [6].

As with the pyroelectric sensors, the performance of the imagers could be enhanced with the improved response and lower NEP of the ultra-thin molecularly engineered LB films. It is true, as Watton points out, that a thinner film yields a higher capacitance in the same material which decreases readout efficiency in vidicons [23]. However, the lower dielectric constants of polymers should allow the use of thinner films.

Reticulation was mentioned as a means to further improve performance by lowering lateral thermal diffusivity. Research in the photoresist area has produced LB films with patterns of 50 nm resolution by writing with an electron beam [102,103]. This degree of resolution would be the ultimate in narrow reticulation.

Optical Applications

The modulation and deflection of guided optical waves was discussed with respect to SAW devices. Actual optical waveguides of piezo- and pyroelectric materials have been investigated since they can provide an active medium for signal processing and integrated optics applications. ZnO seems to be the most popular ceramic investigated due to its transparency at 0.4-2 micron wavelengths, its fairly high refractive index, its high piezoelectricity, and its non-linear optic coefficients. Other ceramics investigated include AlN, KLN, PLZT, LiNbO₃, and LiTaO₃. The standard deposition procedures of CVD and sputtering are the most popular, with the latter being somewhat preferred due to its superior surface quality. Surface quality and thickness control are

most critical for these optical applications [31,37,38,104-106,134].

The LB film deposition method offers many benefits for optical waveguides. Among them are controlled and uniform thickness, uniform molecular orientation, and low temperature deposition. Furthermore, the refractive index can be tailored by merely changing the length of the molecular backbone or adding metal ions. Pitt, who has worked on improving process parameters of ceramic sputtering and investigated their effect on SAW and optical properties of thin films [105], has investigated LB films for use as waveguides with encouraging results [107-109]. Pitt and Walpita measured attenuation in vinyl stearate LB multilayers on the order of 1 dB/cm. They suggested that polymerisable materials might offer films of greater strength and less defects to push this value even lower [135].

Non-linear optical properties of piezo- and pyroelectric materials are also of interest in such areas as second harmonic generation (SHG) and optical displays. Non-linear optical effects have been observed from such widely varied thin film materials as PLLZT [110], PVDF [111,112], and LB deposited films [98,113]. LB films of polydiacetylene have one of the largest known third order non-linear susceptibilities.

Biological Importance

The biological significance of thin piezo- and pyroelectric films is the last area to be mentioned in this review. It is by no means the least important and certainly not the least interesting. Applications in the field

of medical and biological diagnostics have already been mentioned with regard to acoustic imaging and microscopy. Polymers are attractive here due to their close acoustic impedance match with biological tissue and fluids, primarily water. Also, since much of the substance of living organisms is polymeric (DNA and cellulose are macromolecules), polymers are a natural choice for biological compatibility. This has been exemplified by the numerous implants made of plastic materials, the most notable being the artificial heart.

Furthermore, it has been shown that many responses of living organisms and their "components" (such as receptors, skin, plant coatings, etc.) are piezo- and pyroelectric in nature [114,115,132]. Biological piezo- and pyroelectric thin films may control many of our bodily processes. LB technology, besides being compatible with and very suited for polymeric materials, offers the opportunity to build biomembranes, tissue, and biological devices that approach their natural counterparts in chemistry, structure, and function. Sensor and signal processing functions of the body could conceivably be enhanced by such devices. These possibilities have not escaped the recognition of researchers in the LB field [66,129,130].

Conclusions

This rather brief review has attempted to summarize current piezo- and pyroelectric thin film technology and to identify areas where the developing Langmuir-Blodgett film deposition technology may make significant

contributions. The "figures of merit" mentioned for the device applications were primarily film thickness, degree of orientation, surface quality, thickness uniformity, and intrinsic film stress due to the deposition technique. The LB film deposition technique offers advantages for each of these items.

More material-related figures of merit include: dielectric constant, piezo- and pyroelectric coefficients, and thermal diffusivity. The lower coefficients of polymeric materials reduce their response in comparison to the standard materials, but their typically lower thermal diffusivity and dielectric constants help to offset this problem. The low dielectric constant is beneficial in keeping the capacitance from climbing too high as the thickness is reduced. These material properties, and others, need to be determined for candidate LB materials. The flexibility inherent in the LB deposition technique will allow material optimization and ultimately lead to successful device applications.

FIGURE CAPTIONS

1. Piezoelectric and pyroelectric class definitions.
2. Illustrative model of the importance of crystal symmetry [4]. A. Centrosymmetric structure. Each opposing dipole moment changes with strain, but net dipole moment remains zero. B. Non-centrosymmetric structure. Net dipole changes with strain. (Reproduced with permission of publisher and/or author) [4].
3. Simple piezoelectric sensor model.
4. Theoretical relationships between film orientation and coupling modes (K^L - longitudinal, K^S - shear). (Reproduced with permission of publisher and/or author) [13].
5. Relation between piezoelectric d constant and dielectric constant for various polymers. (Reproduced with permission of publisher and/or author) [41].
6. Steps of a monolayer formation and deposition. (Reproduced with permission of publisher and/or author) [131].
7. Some possible types of deposition. A. X-type deposition. B. Y-type deposition. C. Z-type deposition.
8. Effect of film thickness on dielectric constant measurement. (Reproduced with permission of publisher and/or author) [133].
9. Simple bulk wave transducer model. (Reproduced with permission of publisher and/or author) [13].
10. SAW delay line schematic. (Reproduced with permission of publisher and/or author) [80].
11. Optical processor configuration. (Reproduced with permission of publisher and/or author) [78].
12. SAW strain detector test apparatus and test results. (Reproduced with permission of publisher and/or author) [25].
13. Optical guided wave detection using an SAW. (Reproduced with permission of publisher and/or author) [82].
14. SWICC device structure. (Reproduced with permission of publisher and/or author) [86].

15. PIFET configuration. (Reproduced with permission of publisher and/or author) [93].
16. Pyroelectric vidicon schematic. (Reproduced with permission of publisher and/or author) [23].

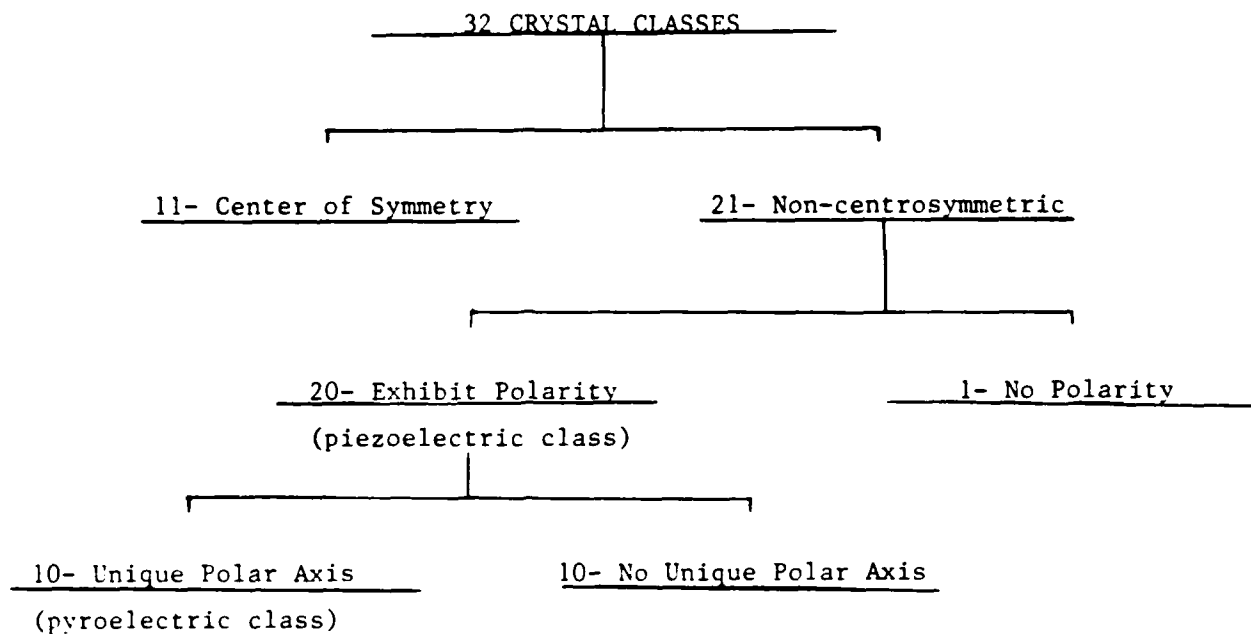


FIGURE 1.

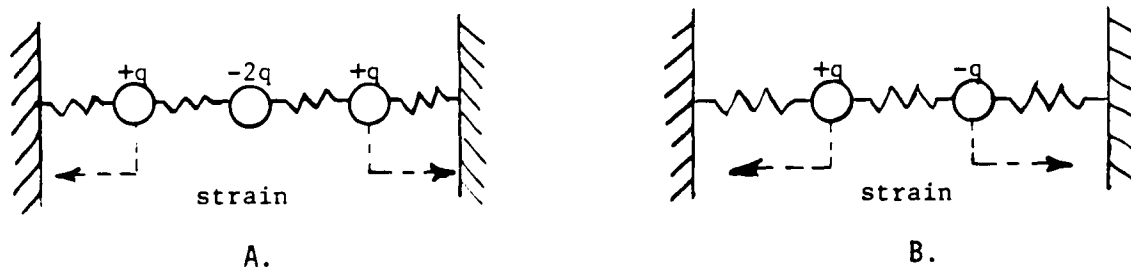


FIGURE 2.

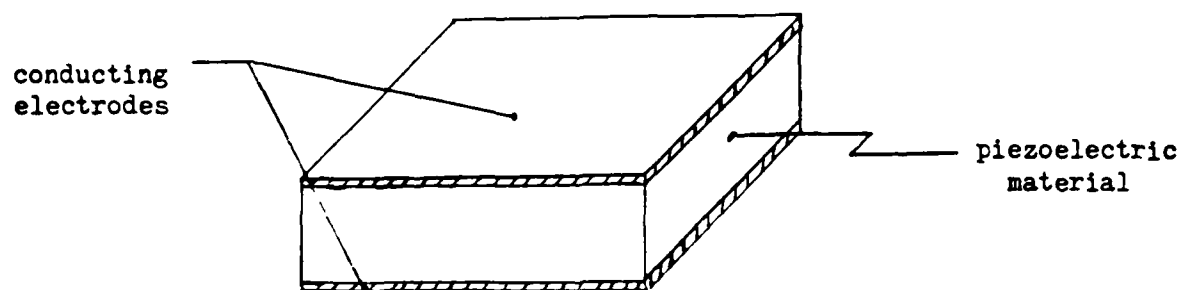


FIGURE 3.

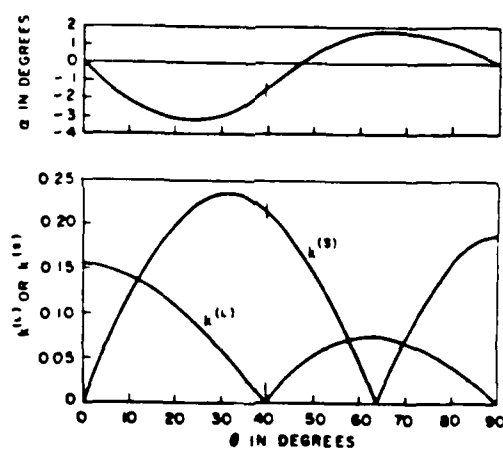


FIGURE 4.

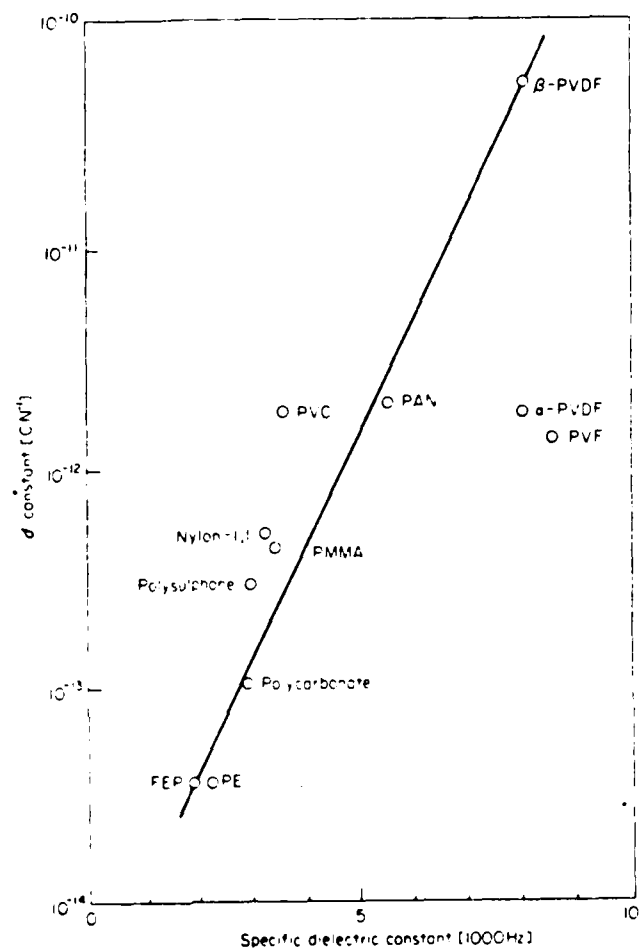


FIGURE 5.

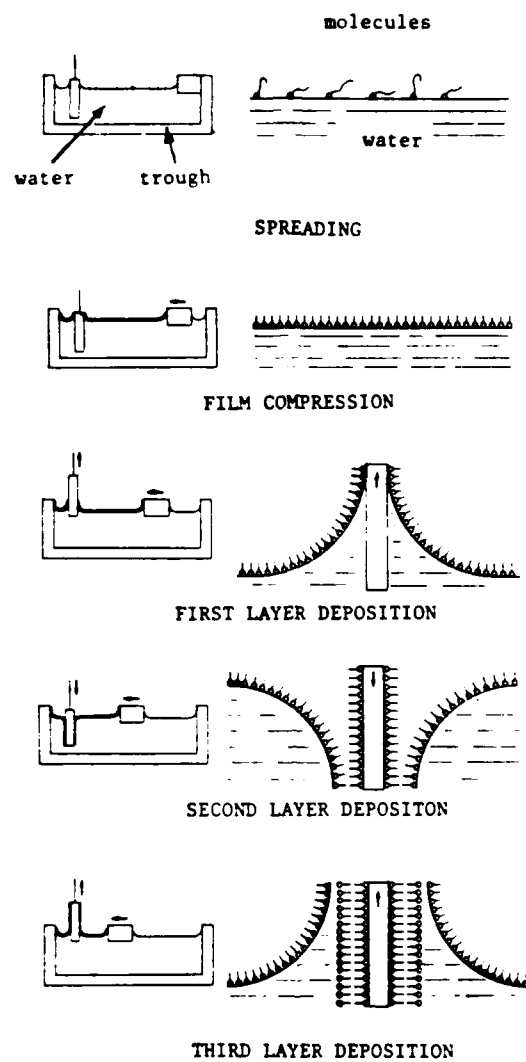
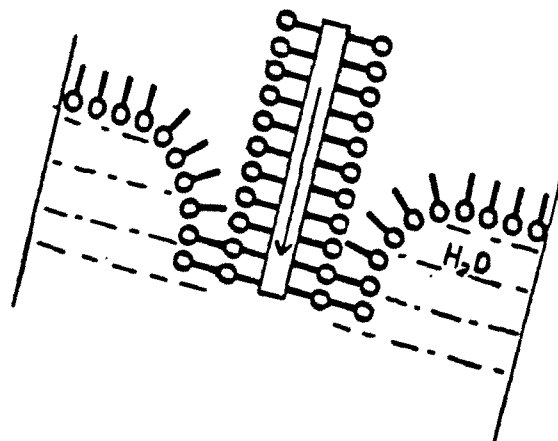
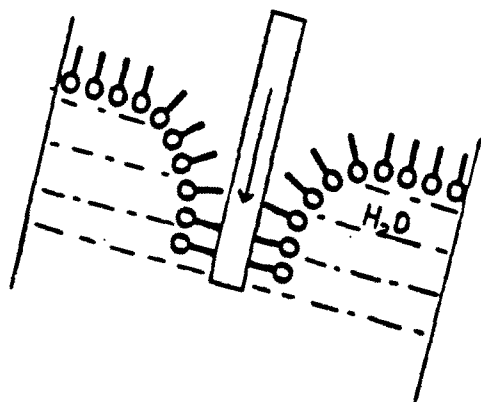
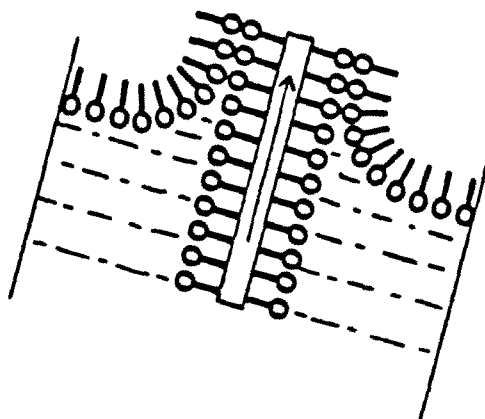
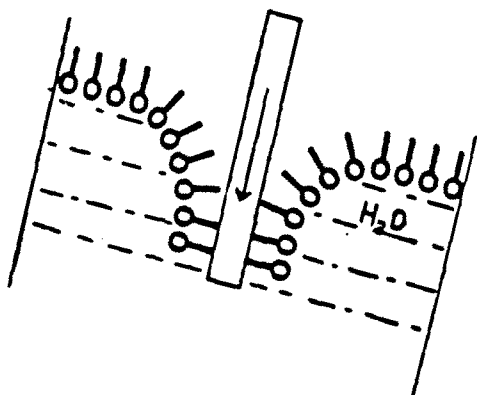


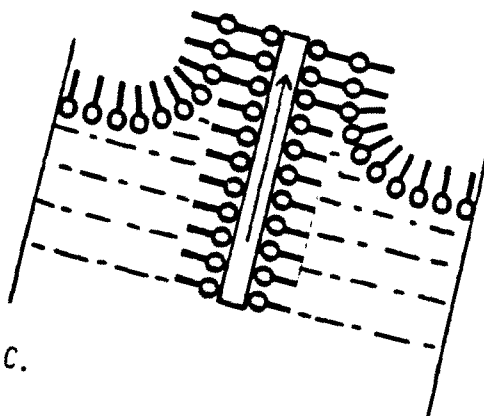
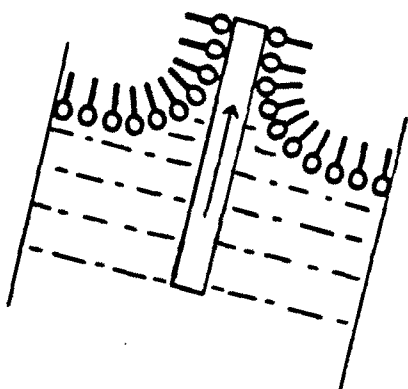
FIGURE 6.



A.



B.



C.

FIGURE 7.

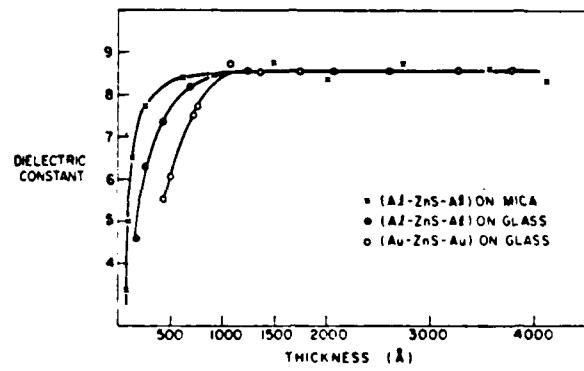


FIGURE 8.

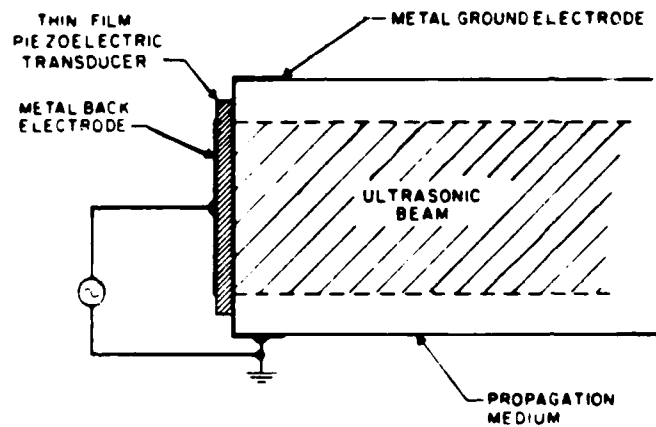


FIGURE 9.

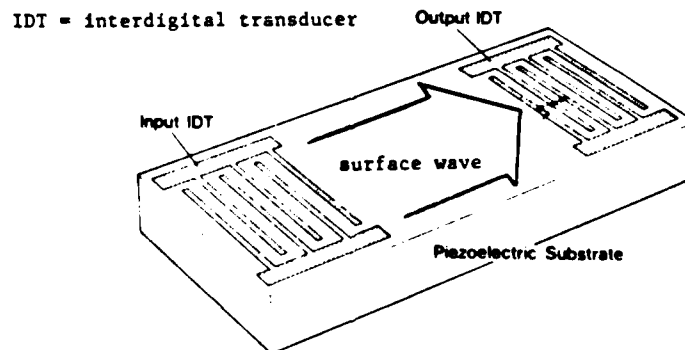


FIGURE 10.

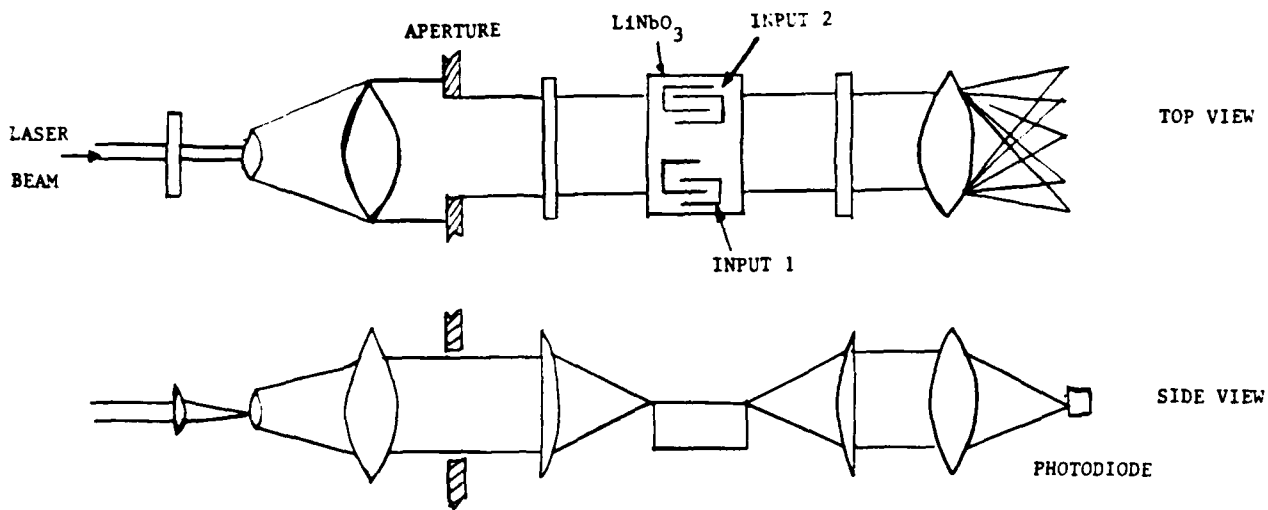


FIGURE 11.

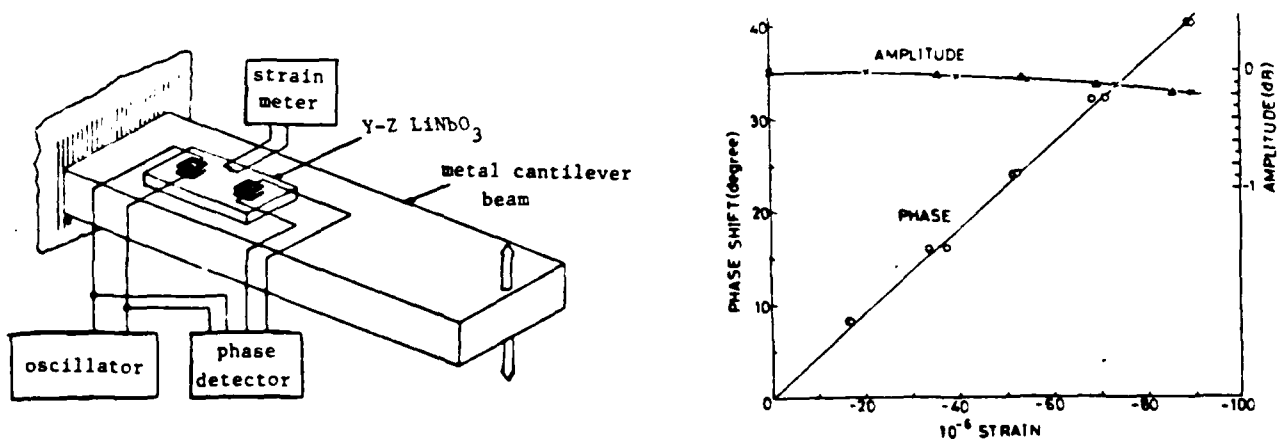


FIGURE 12.

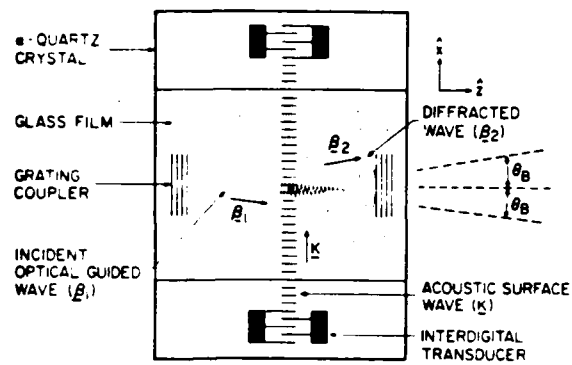


FIGURE 13.

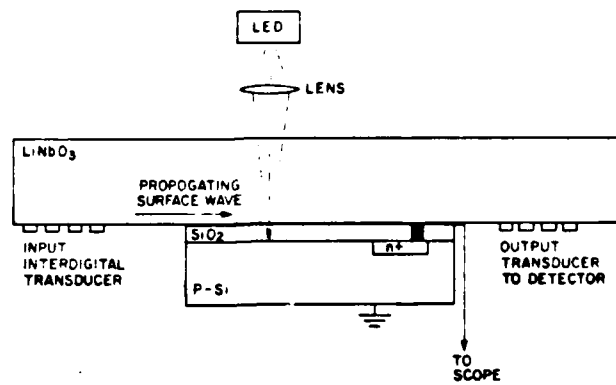


FIGURE 14.

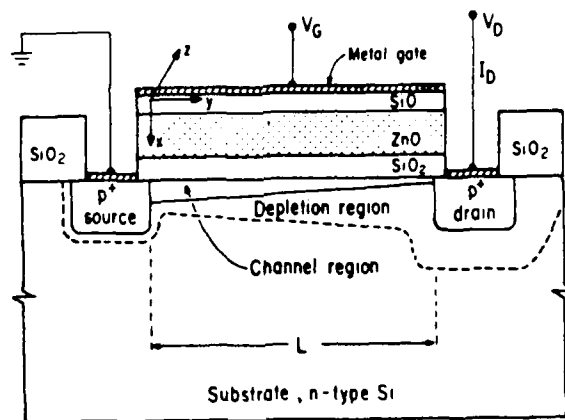


FIGURE 15.

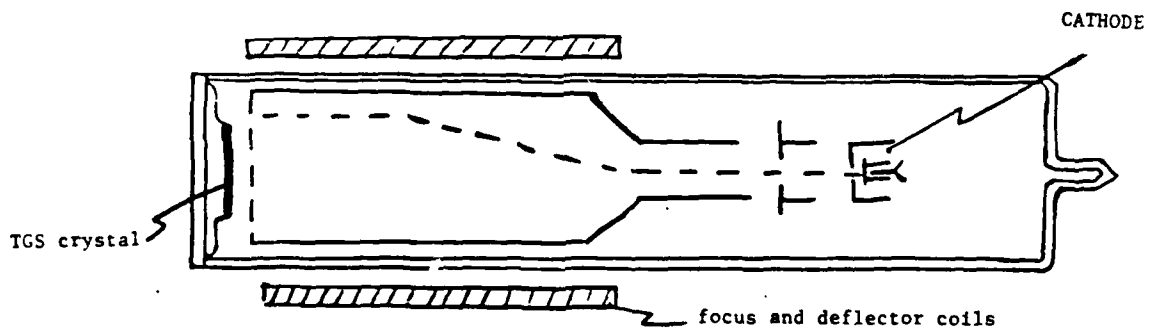


FIGURE 16.

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